1011. *The Conductance of Solutions in which the Solvent Molecule is "Large." Part III.* Amine Picrates in Tritolyl and Tri-(2-ethylhexyl) ("Trioctyl") Phosphates.*

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The conductances of five amine picrates in two phosphoric esters have been examined at 40° in the range $2 \cdot 6 \times 10^{-6}$—$8 \cdot 55 \times 10^{-8}$N. In addition, one of these systems was investigated at 25° and 55°. The conductance of tribenzyl- and triphenyl-ammonium picrates appears to be controlled principally by a molecular dissociation in addition to a limited ionisation. The conductance relationships of the tetraethyl-, tetra-*n*-butyl-, and tetra-*n*-pentyl-ammonium picrates show specific solvent effects. Among the anomalies are an unexpectedly high ion-pair dissociation constant K in tritolyl phosphate; a decrease in K with rise of temperature in trioctyl phosphate; a high ratio for both the dissociation constant and limiting equivalent conductance of tetra-*n*-butyl- to tetraethyl-ammonium picrates; a very low Walden product in trioctyl phosphate, and the appearance of a maximum in the variation of the Walden product with temperature.

FOR conductivity relationships in solutions where the solvent molecule is large it may no longer be possible to maintain that the solvent is an isotropic continuum. Elliott and Fuoss[1] suggested that in such systems the most obvious correction is to allow for the probability that a small ion can pass through certain configurations of large solvent molecules without displacing them. The ion, then subject to much smaller retarding forces than those computed from the observed viscosity, would show a relatively high ionic mobility. The electrical properties of such a discontinuous solvent would probably differ appreciably from those of the idealised medium, and the rôle of the observed, macroscopic dielectric constant may be difficult to assess.

Conductance measurements in such solutions should furnish information on the principles involved in the dynamics of electrolytic conductance not available from similar work with other systems. However, such solvents already examined are restricted to tritolyl phosphate,[1] 2-hydroxyethylamine,[2] 2 : 2′ : 2″-trihydroxytriethylamine, and *N*-ethyl-*N*-2-hydroxyethylaniline,[3] 2 : 2′-dihydroxydiethylamine,[4] and a series of dialkyl phthalates.[5,6] We examined the conductance of more salts in tritolyl phosphate, and extended the range of solvents to tri-(2-ethylhexyl) phosphate and triethyl phosphate (the results for the latter appear anomalous in several respects, and are not presented here).

Elliott and Fuoss[1] and others[7,8] reported that certain amine picrates dissociated both molecularly and ionically in some solvents. Measurements were therefore made with tribenzylammonium and aniline picrates as solutes, in addition to tetraethyl-, tetra-*n*-butyl-, and tetra-*n*-pentyl-ammonium picrates which were used to examine the effect of ion size.

EXPERIMENTAL

Measurements were made and solutes prepared and purified as before.[9] The two solvents were purified as follows: commercial tritolyl phosphate, a mixture of ten isomers with the

* Part II, *J.*, 1957, 2131.

[1] Elliott and Fuoss, *J. Amer. Chem. Soc.*, 1939, **61**, 294.
[2] Briscoe and Dirkse, *J. Phys. Chem.*, 1940, **44**, 388.
[3] Bhattacharyya and Nakhate, *J. Indian Chem. Soc.*, 1947, **24**, 1, 99.
[4] Bhattacharyya and Bhadra, *Current Sci.*, 1947, **16**, 117.
[5] French and Singer, *J.*, 1956, 1424.
[6] *Idem, ibid.*, p. 2428.
[7] Witschonke and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 2472.
[8] Fuoss, Edelson, and Spinrad, *ibid.*, 1950, **72**, 327.
[9] French and Muggleton, *J.*, 1957, 2131.

TABLE 1. *Equivalent conductivity* (X = *picric acid residue*).

Solute	25°		40°		55°	
	10^4c	$10^2\Delta$	10^4c	$10^2\Delta$	10^4c	$10^2\Delta$
	(a) Tritolyl phosphate					
Et₄NX	30·751	7·806	37·552	22·51	32·370	45·16
	27·393	8·063	30·173	23·77	26·176	48·13
	19·716	8·741	26·214	24·13	20·509	51·32
	13·651	9·756	17·993	27·06	13·847	57·56
	10·090	10·94	15·293	28·82	9·9723	62·94
	6·8807	12·51	10·973	32·11	6·0732	71·99
	5·4684	13·26	7·4824	36·64	5·0436	75·81
	3·7707	15·00	5·8592	39·62	4·4129	77·91
	1·6789	18·59	3·6615	46·89	2·5006	88·27
	1·4948	19·26	2·0527	55·50	1·1054	101·0
	0·64860	22·51	1·2484	62·14	0·87997	105·1
	0·49608	23·61	0·92010	68·65		
	0·11370	27·36	0·40103	75·74		
			0·15544	84·73		
	(b) Trioctyl phosphate					
Et₄NX	6·4148	4·602	5·5970	7·954	5·6093	13·47
	5·1534	4·900	2·9879	11·24	3·6164	15·91
	3·0812	5·963	2·6964	11·87	3·3442	16·26
	2·5793	6·470	1·1835	18·07	2·0999	19·50
	1·5161	8·198	0·66578	22·01	1·5252	22·89
	0·84168	10·66	0·44652	24·84	0·83198	29·97
	0·58349	12·25	0·23149	32·12	0·70252	32·11
	0·52914	12·92	0·12826	41·25	0·56427	34·55
	0·25031	16·81	0·10130	44·76	0·34781	42·49
	0·21448	18·13			0·20759	51·90
	0·11478	21·94			0·16225	57·70
					0·08377	71·62
					0·042304	93·44
					0·025998	103·52

Solute	(c) Tritolyl phosphate at 40°				Trioctyl phosphate at 40°			
	10^4c	$10^2\Delta$	10^4c	$10^2\Delta$	10^4c	$10^2\Delta$	10^4c	$10^2\Delta$
Bu₄NX	85·549	16·30	9·3248	27·08	43·341	5·812	1·4766	18·46
	80·593	16·49	7·2498	29·30	22·765	6·520	0·85224	23·23
	49·434	17·78	5·6093	31·31	18·741	6·842	0·51017	28·74
	38·703	18·50	2·9587	35·72	13·584	7·587	0·26308	40·15
	28·046	20·00	2·0355	37·88	6·2888	10·14	0·11166	52·32
	24·196	20·70	1·7642	39·09	3·3790	13·21		
	18·675	22·49	1·2916	40·49				
	12·857	24·78	0·21523	46·42				
(C₅H₁₁)₄NX	59·761	16·49	7·6663	28·38	46·909	5·125	2·6137	13·67
	41·202	17·78	5·8725	30·44	33·699	5·473	1·3140	18·69
	33·653	18·85	5·4790	31·40	24·259	5·938	0·70565	24·49
	31·746	19·12	4·0743	32·67	14·223	7·020	0·43985	30·35
	23·758	20·68	2·3991	36·00	6·7702	9·002	0·21176	43·06
	18·908	22·07	1·1855	39·59	4·4568	10·72	0·12147	52·44
	14·326	23·71	0·65966	42·01				
	9·4396	26·68	0·15338	45·81				
(Ph·CH₂)₃NHX	32·503	7·792	3·8124	12·86	17·862	3·215	0·59342	4·896
	28·386	8·097	1·2601	15·19	13·487	3·442	0·28078	6·442
	22·794	8·433	0·59406	17·56	6·1057	3·941	0·16491	8·616
	13·997	9·741	0·39791	17·94	5·1082	4·004	0·14057	9·741
	8·8215	10·82	0·20751	22·44	1·9653	4·313	0·079347	12·67
	6·7745	11·57			0·98992	4·592		
Ph·NH₃X	59·671	1·635	5·3712	3·312	76·573	0·6567	4·3735	1·862
	44·053	1·787	5·1220	3·349	51·854	0·7624	2·6534	2·232
	34·344	1·920	3·8825	3·611	29·486	0·8816	1·9187	2·500
	26·474	2·084	2·0274	4·419	23·520	0·9610	1·3883	2·746
	19·211	2·284	1·9751	4·320	13·991	1·219	0·64398	3·555
	13·912	2·528	0·70683	5·481	10·724	1·329	0·43696	4·061
	7·9596	2·975			6·1661	1·631	0·22102	4·876

purely *ortho*-form predominating, was kept for some weeks over dried calcium chloride, then distilled through a well-lagged column at a pressure of 4 mm., initial and final fractions (10% of the whole) being rejected. The pale yellow liquid was twice redistilled under reduced pressure, the final product being a colourless oil stable to light. The physical constants depend on the proportion of isomers present; those now recorded were sensibly constant from batch to batch and corresponded to a product consisting largely of the purely *ortho*-ester (literature values may refer to mixtures with somewhat different proportions of the isomers), b. p. 232—234°/4 mm.; n_D^{20} 1·56703; d_4^{25} 1·16484, d_4^{40} 1·15307, d_4^{55} 1·14146; dielectric constant: ε_{25} 6·73, ε_{40} 6·14, ε_{55} 5·47; viscosity (in centipoises): η_{25} 138·6, η_{40} 70·06, η_{55} 36·48; specific conductivity: κ_{25} 2·31 × 10^{-12}, κ_{40} 4·17 × 10^{-12}, κ_{55} 5·23 × 10^{-12} (lit.: b. p. 270—275°/10 mm.,[1] n_D^{20} 1·5573,[1] d_4^{25} 1·1590, d_4^{40} 1·1445, d_4^{55} 1·1304,[1] η_{20} 155·1[10]).

Tri-(2-ethylhexyl) phosphate (" trioctyl " phosphate) mixed with its own volume of ether was shaken with 5% hydrochloric acid and the organic phase filtered to remove traces of pyridine hydrochloride (pyridine was a solvent during manufacture), then shaken with sodium carbonate solution, then water, and the ether distilled off, and the ester filtered. The phosphate was then dried for 12 hr. at 100°/15 mm., and traces of solid filtered off. The now colourless ester was next intermittently shaken for 48 hr. with activated alumina (100 g./l.), stored overnight, and decanted through a fine sintered-glass disc, care being taken to exclude moisture. The phosphate was then fractionated and finally twice distilled at 3—4 mm. pressure, generous head and tail fractions being rejected (b. p. 204°/3·2 mm., 219°/5 mm.; n_D^{20} 1·44464; d_4^{25} 0·92042, d_4^{40} 0·90934, d_4^{55} 0·89766; ε_{25} 4·72, ε_{40} 4·53, ε_{55} 4·26; η_{25} 27·21, η_{40} 16·63, η_{55} 11·05; κ_{25} 4·38 × 10^{-11}, κ_{40} 9·07 × 10^{-11}, κ_{55} 13·76 × 10^{-11} (lit.: b. p. 220°/5 mm.,[2] n_D^{20} 1·443,[2] d_{20}^{20} 0·924[2]).

Results.—The variation in equivalent conductance with concentration in the ten systems is shown in Table 1.

DISCUSSION

The conductimetric behaviour exhibits interesting features, and suggests the intervention of specific solvent effects. The chief points requiring explanation are now discussed.

The Fuoss plots for all three tetra-alkylammonium salts in both solvents were linear, and values of the limiting equivalent conductance, Λ_0, and the dissociation constant, K, obtained from them are given in Table 2. In view of the dielectric constant of both solvents (*ca.* 5), the solutes should behave as weak electrolytes, and this is confirmed for solutions in trioctyl phosphate by the values of K. In tritolyl phosphate, however, the dissociation constants are as large as in solvents of higher dielectric constant, *e.g.*, ethylene

TABLE 2.

Solute	Temp.	Tritolyl phosphate			Trioctyl phosphate		
		$10^4 K$	Λ_0	$\Lambda_0\eta$	$10^6 K$	Λ_0	$\Lambda_0\eta$
Et$_4$NX	25°	0·916	0·316	0·438	3·21	0·513	0·139
	40	0·900	0·987	0·691	0·905	1·63	0·271
	55	1·044	1·51	0·581	0·173	1·88	0·208
Bu$_4$NX	40	7·81	0·508	0·357	5·97	0·975	0·162
(C$_5$H$_{11}$)$_4$NX	40	8·85	0·493	0·347	6·43	0·925	0·153

dichloride [11] (ε = 10·23 at 25°; K × 10^5 for tetraethyl-, tetra-*n*-butyl- and tetra-*n*-pentyl-ammonium picrates = 15·9, 22·6, and 23·8 respectively). These results are consistent with the shape of the Λ–$c^{\frac{1}{2}}$ plots which for solutions in trioctyl phosphate are typical of weak electrolytes and rise steeply at low concentrations, indicating extensive ion-pair formation. The corresponding curves for solutions in tritolyl phosphate are relatively shallow, however, and tend towards the straight-line plots obtained with strong electrolytes. Contrary to expectation the Λ–$c^{\frac{1}{2}}$ plots exhibit no minimum in the more concentrated region, although triple-ion formation might be expected at about 3 × 10^{-3}N. The absence of triple ions is confirmed by the non-linearity of the $\Lambda c^{\frac{1}{2}}$–c plots.

[10] Buttrey, " Plasticizers," Cleaver-Hulme Press, London, 1950.

The dissociation constants of these salts decrease with increase in cation size as in most solvents, but in contrast to their behaviour in acetonitrile.[9] Of particular interest too is the ratio of the dissociation constants of pairs of salts. The ratio for tetrapentyl- to tetrabutyl-ammonium picrate is similar to that in other solvents, but the ratio for tetra-n-butyl- to tetraethyl-ammonium picrate is very high (8·67 in tritolyl and 6·56 in trioctyl phosphate at 40°; cf. 1·42 in ethylene dichloride,[11] 1·30 in ethylidene chloride,[12] 1·16 in ethyl alcohol [13] at 25°). This suggests that specific solvent effects operate here.

The effect of temperature on the dissociation constant is not uniform, but again indicates specific solvent effects and the general complexity of factors involved. Kraus [14] pointed out that, according to Bjerrum's equation, K in solvents of low dielectric constant should increase with temperature since the dielectric constant ε changes little and εT increases. In tritolyl phosphate, however, ε decreases with rise in temperature, and there is moreover an overall decrease in εT from 25° to 55°. In trioctyl phosphate the decrease in ε with temperature rise is small and may not be significant: εT shows little change. Whereas in trioctyl phosphate there is a progressive decrease in dissociation constant with increase in temperature, consistent with the overall change in dielectric constant, but in contradiction to Kraus's suggestion, in tritolyl phosphate the dissociation constant changes little, but passes through a minimum. Perhaps in the latter solvent the opposing effects of increased kinetic energy and decreased dielectric constant with rise of temperature are nearly but not completely balanced.

The relative magnitudes of the limiting equivalent conductances of the tetra-alkyl-ammonium picrates in the two phosphoric esters (Table 2) are similar to those of the dissociation constants. Whereas in solvents with relatively small molecules Λ_0 for the quaternary ammonium salts decreases fairly regularly with increase in cation size—an effect attributable to the increasing influence of viscosity on the larger solute ions—in both phosphates Λ_0 for tetraethylammonium picrate is very much greater than that for tetra-n-butylammonium picrate, the ratio for these two salts being 1·94 in tritolyl phosphate and 1·67 in trioctyl phosphate compared with approximately 1·2 in more conventional solvents. Thus the tetraethylammonium ion appears to be unexpectedly more mobile than other tetra-alkylammonium ions in these solvents.

The constancy of the Walden product may be taken as an indication of the extent to which ion size remains unchanged in different solvents. The magnitude and irregular variation in $\Lambda_0\eta$ for the tetra-alkylammonium picrates in the two phosphoric esters (Table 2) is therefore of interest. Thus in tritolyl phosphate at 40° the Walden product for tetraethylammonium picrate is more than 20% higher than its " normal " value of 0·560, and is nearly twice as great as $\Lambda_0\eta$ for the other two picrates which are correspondingly over 30% lower than " normal." In trioctyl phosphate $\Lambda_0\eta$ for tetraethyl-ammonium picrate is again considerably greater than for the two higher homologues, but all are much less than the " normal " value. It is curious that the Walden products for tetra-n-butyl- and tetra-n-pentyl-ammonium picrates in the latter solvent are lower than $\Lambda_0\eta$ for the picrate ion in normal solvents, e.g., 0·255 in ethylene dichloride [11] and ethylidene chloride,[12] 0·269 in methyl alcohol,[13] and the significance of this is not apparent. The particularly low mobilities in trioctyl phosphate might be due to extensive ion solvation in the sense of a loose association between an ion and solvent molecules. The magnitude of this effect could be different in the two phosphoric esters, tritolyl phosphate being a relatively compact molecule and trioctyl phosphate a large one with an exposed polar group at one end. It then appears that in both solvents the tetraethylammonium ion was less solvated than its two higher homologues, although this is unusual since small, highly polar ions are more likely to be highly solvated than those whose size results in

[11] Tucker and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 454.
[12] Healey and Martell, *ibid.*, 1951, **73**, 3296.
[13] Evers and Knox, *ibid.*, p. 1739.
[14] Kraus, *J. Phys. Chem.*, 1956, **60**, 129.

considerable reduction of surface electrostatic charge density. An alternative hypothesis that the tetraethylammonium ion represents the "small" ion of Elliott and Fuoss's theory [1] does not seem tenable, particularly since at 25° $\Lambda_0\eta$ for this picrate also is less than the usual value.

The only direct comparison at present possible with conductance measurements in other systems with large solvent molecules is with Elliott and Fuoss's results [1] on tetra-*n*-butylammonium picrate in tritolyl phosphate. These are very different from ours. Elliott and Fuoss obtained a high Walden product for this solute, and found that it behaved as a weak electrolyte. The reason for these apparent discrepancies is not known, the only obvious difference between the two investigations lying in the method of purification of the solvent. The high mobility obtained for tetra-*n*-butylammonium picrate by Elliott and Fuoss, and which corresponds to that of tetraethylammonium picrate in tritolyl phosphate obtained now, was ascribed by them to a slipping of ions between solvent molecules in certain configurations, but we believe that this is too facile an explanation. The behaviour of solutes in solvents with large molecules appears complex, and may well be governed by specific solvent effects.

The effect of temperature on the Walden product is also of interest: $\Lambda_0\eta$ should vary little with temperature if ion size remains unaltered; however, for reasons suggested earlier,[5] the degree of solvation might decrease with increasing temperature, so that the mobility of the ions should increase. The Walden product increases with temperature for a series of dialkyl phthalates as solvents,[5] but in both phosphoric esters, with rise in temperature, $\Lambda_0\eta$ first increases, passes through a maximum, and finally decreases. This is related to the fact that the increase in Λ_0 with temperature is less than linear. Although initially the increase in Λ_0 with temperature exceeds the decrease in viscosity so that $\Lambda_0\eta$ increases, a temperature is eventually reached at which the viscosity change outweighs the conductance change, and $\Lambda_0\eta$ subsequently decreases. It is possible, moreover, that the macroscopic, bulk viscosity of solvents of this type with large molecules, in no way represents the viscosity in the neighbourhood of the ions of tetra-alkylammonium picrates, and that Walden's rule, using this observed viscosity, cannot therefore be applied.

The behaviour of tribenzylammonium and aniline picrates in the two phosphoric esters is similar to that in acetonitrile [9] and other solvents. The values of Λ_0 for the two solutes in both solvents, obtained from the Fuoss plots, are very low. This suggests that, as in a number of other solvents, the behaviour of both these picrates in the two phosphoric esters is governed largely by an acid–base, *i.e.*, molecular, dissociation in addition to a small ionic dissociation.

Much more information is required to explain the conductance relations in solvents with large molecules, and further work is in progress.

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